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# The Influence of the Bleaching Medium on Caustic Extraction Efficiency (II): Oxidized Lignin Solubility

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# THE INFLUENCE OF THE BLEACHING MEDIUM ON CAUSTIC EXTRACTION EFFICIENCY (II): OXIDIZED LIGNIN SOLUBILITY

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## ABSTRACT

Caustic extractions performed with >50% (v/v) ethanol or >0.0025 mol/L aqueous $BaCl_2$ severely hindered lignin removal from chlorine dioxide ($D_0$) treated pulps. The solubility of alkali-treated $D_0$-stage lignins was measured in various ethanol-water and $BaCl_2$ solutions at alkaline conditions to determine if solubility limits delignification. Oxidized lignin solubility decreased as the concentration of ethanol or $BaCl_2$ was increased. The amount of dissolved lignin in the alkaline extraction effluents approached the solubility limit of the corresponding medium when high concentrations of ethanol (>50%) were present. A similar relationship was observed with the aqueous $BaCl_2$ system when the Donnan effect is considered. The results suggested that alkaline extractions of $D_0$ pulps with media rich in ethanol or $BaCl_2$ were related to the lower solubility of ionized lignin fragments in these solutions compared with a totally aqueous medium.

## INTRODUCTION

Many process modifications have been developed, and will continue to be developed, to produce strong, fully bleached pulps with minimum impact on the environment. Since more stringent emission regulations are anticipated, future legislation may require revolutionary changes to our current bleaching technologies. Of particular interest for us is the application of organic solvent-water solutions during pulping and bleaching [1-4]. Substitution of organic solvent-water solutions for water may provide a selective process for removing residual lignin while producing high brightness chemical pulps with minimum water usage. Recent studies of ozone bleaching have indicated that bleaching selectivity can be greatly improved by employing an organic solvent-water solution instead of water as the impregnating medium [3,4]. Nevertheless, the use of non-aqueous media for other oxidative and/or extraction stages has not been studied.

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We have investigated ethanol-based caustic extractions (E) of softwood kraft brownstocks previously treated by a chlorine dioxide ($D_0$) stage [5]. Our studies have shown that delignification was severely inhibited when the ethanol concentration in the alkaline extraction medium was increased from 50 to 85% (v/v). A similar effect was also observed when the $BaCl_2$ concentration was increased from 0.0025 to 0.01 mol/L in the aqueous alkaline extraction medium. It was initially hypothesized that the decreased delignification with these systems was caused by the reduced mobility of lignin fragments within the fiber wall as a result of fiber deswelling. However, alkaline extraction experiments conducted with aqueous NaCl solutions and with air-dried $D_0$-treated pulps yielded results indicating that reduced fiber swelling has a minor effect on E-stage lignin removal. Furthermore, qualitative analyses on the sizes of fiber pores and lignin fragments indicated that the reduction in pore sizes caused by fiber deswelling should not severely inhibit the removal of oxidized lignin fragments.

The decrease in delignification efficiency of E-stages conducted in ethanol-water or aqueous $BaCl_2$ solutions may be the result of low oxidized lignin solubility in these media. In this paper, we examine the solubility of the alkali-treated $D_0$-stage lignin in various ethanol-water and aqueous $BaCl_2$ solutions in order to determine if the solubility of oxidized lignin limits extraction delignification in these media.

## RATIONALE AND METHODOLOGY

If lignin solubility limits E-stage delignification when ethanol-water or aqueous $BaCl_2$ solutions are used, then several effects should be observed. The solubility of an isolated, $D_0$ lignin should decrease when the solvent composition is progressively changed from water to absolute ethanol. A similar decrease in solubility should also be observed when the $BaCl_2$ concentration in an aqueous medium is increased. The solubility of the oxidized lignin in the various media can be compared to the amount of dissolved lignin in the effluent of the corresponding extraction. A dramatic decrease in lignin solubility should occur at the ethanol or $BaCl_2$ concentration where E-stage delignification was observed to sharply decrease. If solubility limits E-stage delignification in ethanol-water or aqueous $BaCl_2$ media, then additional lignin should be removed when these pulps are washed and re-extracted in a totally aqueous medium, provided that the lignin fragments have not been irreversibly bonded to the pulp.

## LIGNIN SOLUBILITY AND CONCENTRATION IN EXTRACTION EFFLUENTS

*Isolated Oxidized Lignin*

A conventional unbleached softwood kraft pulp was subjected to a chlorine dioxide delignification stage; afterwards, the pulp was treated with aqueous caustic extraction stage. The resulting extraction effluent was freeze-dried to afford the oxidized lignin used in the present study. Solubility measurements of this alkali-treated $D_0$-lignin were made in the various ethanol-water and $BaCl_2$ solutions at a typical E-stage alkali concentration based on our previous study (0.071 mol/L NaOH, [5]). An analysis showed that the isolated oxidized lignin contained ≤7% (w/w) carbohydrate material. The small amount of carbohydrates in the isolated lignin is comparable to that recently reported by Fuhrmann *et al.* [6] in $ClO_2$-based bleaching effluents. The carbohydrates in the alkali-treated $D_0$-lignins could have come from the degradation and solubilization of hemicelluloses during extraction [6,7], and/or from carbohydrates covalently bonded to the extracted lignin [7-9].

*Solubility of Isolated Oxidized Lignin*

Several attempts were made to measure the solubility of the oxidized lignin in water. However, the modified lignin was so soluble in aqueous alkali that it had not reached the saturation limit even when the concentration was increased to 22 g/L (Table I). Additional experiments to determine the solubility of this lignin in water were not performed due to the limited amount of the isolated lignin available.

The solubility of the oxidized lignin in ethanol-water decreased by ~10-fold as the ethanol content was increased from 50 to 75%. It was very sparingly soluble in absolute ethanol. Increasing the $BaCl_2$ concentration in aqueous solutions also decreased the solubility of the lignin (Table II). The solubility decreased by ~75% as the $BaCl_2$ concentration was increased from 0.0100 to 0.0175 mol/L. Higher concentrations of $BaCl_2$ (>0.0175 mol/L) in the aqueous solution marginally decreased the solubility of the oxidized lignin.

*Oxidized Lignin Concentration in Extraction Effluents*

Table III displays the concentration of oxidized lignin, [L], observed in the medium consistency E-stage effluents performed with various ethanol and $BaCl_2$ solutions. The amount of oxidized in the effluents decreased sharply as the ethanol concentration was increased above 50% or as the $BaCl_2$ concentration was increased from 0.0025 to 0.01 mol/L (Table IV).

## COMPARISONS OF SOLUBILITY LIMITS WITH E-STAGE DELIGNIFICATION

The presence of high concentrations of ethanol (>50%) or $BaCl_2$ (>0.0025 mol/L) adversely affected the alkali solubility of the oxidized lignin. Comparisons between the measured lignin solubility and concentration in the E-stage effluents and the measured post-extraction kappa numbers of the pulp in the various media indicate that solubility effects are limiting delignification (Figures 1 and 2). The [L] in the E-stage effluents (curve B) and the kappa numbers (curve A), as shown in these figures, are complementary: as the kappa number decreases, [L] increases. At high ethanol and $BaCl_2$ concentrations, [L] and the oxidized lignin solubility (curve C) coincide.

Interestingly, the [L] levels in the E-stage effluents with >50% ethanol were at the measured solubility limit. The post-extraction kappa number increased sharply just as lignin solubility decreased abruptly. The [L] level in the 50% E-stage effluent approached the saturation limit of the oxidized, alkali-treated $D_0$-lignin, indicating that solubility limits delignification at higher ethanol concentrations.

Unlike the ethanol-water system, the [L] levels in the E-stage effluents with 0.005 to 0.010 mol/l $BaCl_2$ did not appear to approach the solubility limit just as the post-extraction kappa increased abruptly. The increase in the kappa number and the reduction of [L] levels was expected to start at $BaCl_2$ concentrations of ~0.0175 mol/L on the basis of previously determined solubility measurements. Instead, the extraction efficiency sharply decreased when the $BaCl_2$ levels were increased from 0.0025 to 0.010 mol/L. This discrepancy between the abrupt decrease in oxidized lignin solubilities and the sharp rise in kappa numbers may be related to an unequal concentration of mobile ions in the bulk solution and in the interstitial fluid of the fiber wall.

The immobile carboxylic anions in the pulp fibers, according to the Donnan theory for ionized gels [10,11], should cause the concentration of $Ba^{+2}$ ions, $[Ba^{+2}]$, to be higher inside the fibers than outside. Estimates of $[Ba^{+2}]$ inside the fiber, using a simple Donnan model [12], were calculated to be 0.0084 and 0.015 mol/L during an E-stage with 0.005 and 0.01 mol/L $BaCl_2$ media, respectively. Indeed, the decrease in lignin solubility in 0.0100 to 0.0175 mol/L $BaCl_2$ solutions closely parallels the reduction in [L] levels observed with 0.0050 to 0.0100 mol/L $BaCl_2$ in the extraction media. Higher $[Ba^{+2}]$ levels inside the fiber probably decrease the solubility of oxidized lignin in the interstitial fluid of the fiber, which consequently limits lignin dissolution and extraction from the fiber wall.

## RE-EXTRACTION OF E-STAGE PULPS WITH AN AQUEOUS MEDIUM

Previously, it was shown that an ethanol-based E-stage and subsequent ethanol wash resulted in ~3 unit kappa number reduction of a $D_0$-treated pulp (Fig. 3) [5,12]. Several additional tests were performed with the pulp extracted with the 100% ethanol E-stage to further examine the oxidized lignin solubility issue. Washing the ethanol E-stage pulp with deionized (DI) water instead of ethanol resulted in ~4 unit kappa number drop, from 16.3 to 12.1. Performing a second E-stage on this DI washed pulp in an aqueous medium decreased the kappa number to the same level observed with an aqueous E-stage on a $D_0$-treated pulp. The kappa number reduction of the ethanol-based E-stage pulp during washing and re-extraction in water indicates that the oxidized lignin has not been irreversibly bonded to the fiber. Clearly, these results also suggest that delignification with an ethanol-based E-stage is limited by the solubility of oxidized lignin in ethanol-rich media.

Some additional washing and extraction experiments, similar to the tests with ethanol E-stage pulp, were performed with the 0.01 mol/L $BaCl_2$ E-stage pulp (Fig. 4). Washing the pulp with DI water instead of an aqueous 0.01 mol/L $BaCl_2$ solution did not cause a significant decrease in the lignin content of the pulp. A second E-stage performed on this pulp with an aqueous medium resulted in 3.1 kappa number reduction. It should be pointed out, however, that the aqueous washing between the two E-stages does not completely remove all the $Ba^{+2}$ in the pulp. Thus, some of the 0.01 mol/L $BaCl_2$ E-stage pulp was treated with an acid-wash stage to ion exchange the $Ba^{+2}$ in the pulp with $H^+$. This acid-wash treatment resulted in a unit reduction in the kappa number of the pulp. When a second E-stage was performed on this acid washed pulp, the kappa number decreased from 13.1 to 8.6. Again, it appears that the caustic extraction of $D_0$ pulp in 0.01 mol/L $BaCl_2$ did not cause the oxidized lignin to be permanently bonded to the fiber wall. These results indicate that oxidized lignin solubility also limits E-stage delignification in the presence of high levels of $Ba^{+2}$.

## LITERATURE OBSERVATIONS ON LIGNIN SOLUBILITY AND EXTRACTION

The solubility behavior of oxidized lignins and the lignin extraction efficiencies in aqueous $BaCl_2$ solutions appear consistent with several reports. Kraft lignins have been shown by Lindström [13] to coagulate and precipitate from aqueous solutions when the $BaCl_2$ concentration reached 0.002 to 0.008 mol/L. Li and MacLeod [14] have also reported that alkaline leaching of lignin from kraft brownstocks was inhibited when the aqueous leaching solutions contained >0.001 mol/L $BaCl_2$. The authors attributed the lower levels of

delignification to $Ba^{+2}$ promoting the coagulation of kraft lignin. In addition, $Ba^{+2}$ ions are reported to form "ionic cross-linkages" between carboxylic anions [15]; such ionic cross-linkages could increase the hydrodynamic volume of oxidized lignin [7] via coagulation and decrease the solubility of the lignin in aqueous solutions.

The solubility of oxidized lignin in ethanol-water solutions, however, differs from what one might initially expect based on the reported behavior of organosolv lignins. Ni and van Heiningen [2] have shown that additional lignin can be leached from Alcell® brownstocks if the pulps are washed with aqueous ethanol solutions containing >50% (w/w) ethanol instead of water. This washing medium corresponds closely with the observed maximum solubility of Alcell® lignins in ethanol-water solutions (~70% (w/w)) [16].

The apparent discrepancy between the solubility behavior of Alcell® lignin and alkali-treated $D_0$-stage lignin could be explained by the alkalinity that prevails in the latter case. Ethanol leaching of Alcell® pulps is conducted at slightly acidic to neutral conditions [2], whereas the caustic extractions performed in this study were conducted at high alkalinities (0.071 mol/L NaOH). Unlike kraft or organosolv lignins, $D_0$-lignins have been extensively modified, and contain more carboxylic acid and fewer methoxyl groups [17]. Under alkaline conditions of the E-stage, the carboxylic acids contained in the oxidized lignin are converted to their sodium salts. Sodium salts of carboxylic acids are generally less soluble in organic solvents than their protonated forms (Table V) [18,19]. These sodium salts are typically more soluble in water than in absolute ethanol. Apparently, the ionized carboxylic acids impart increased hydrophilicity to the oxidized lignin under alkaline conditions. Lignosulfonates, which contain ionized sulfonic acid groups, also exhibit similar solubility behavior similar to that of ionized $D_0$ lignins (i.e., lower solubility in organic solvents or solvent-water solutions as compared to water) [20,21]. The higher solubility of lignin with ionized acid groups in water versus non-aqueous media is probably related to the medium's ability to stabilize ionized polar groups [22].

The data in Table V indicates that carboxylic acids, in their undissociated form, are generally more soluble in ethanol than in water. Oxidized lignin may likewise be more soluble and extractable in an acidic, ethanol-rich medium than in water. Most organic solvent-based pulping processes utilize acidic to neutral media in order to extract lignin from wood [1]. In subsequent studies, we examined the extraction of $D_0$-treated pulps with acidic ethanol-water solutions [23], and the impact of this novel extraction stage on future pulp bleachability [24].

## CONCLUSIONS

Solubility measurements of kraft $D_0$-stage lignin in various ethanol-water and aqueous $BaCl_2$ solutions were conducted on dissolved oxidized material that was isolated from an aqueous caustic extraction stage. The solubility of oxidized lignin under alkaline conditions sharply decreases as the ethanol concentration is increased from 50 to 75%, and as the $BaCl_2$ concentration is increased from 0.010 to 0.025 mol/L. The rapid reduction in oxidized lignin solubility corresponds well with observed lignin concentration, [L], in alkaline extraction effluents with ethanol-water solutions. The slight discrepancy between lignin solubility and [L] levels in alkaline extraction effluents with $BaCl_2$ solutions can be reconciled if the Donnan effect is considered. The decrease in extraction efficiency with ethanol-water or aqueous $BaCl_2$ solutions, as observed in the previous study [5], appears to be limited by the alkali solubility of oxidized lignin in these media.

There are some important implications from this study that can apply to pulp bleaching. First, an E-stage designed to remove lignin after an oxidative stage (e.g., $D_0$ or Z) will be ineffective at lignin removal if the extraction medium contains high concentrations of an organic solvent, such as ethanol. However, the expected solubility behavior of carboxylic acids suggests that oxidized lignin will be more soluble in ethanol-water solutions than in water under acidic conditions. Future studies will examine acid extraction of $D_0$-treated pulps with ethanol-water solutions. A second important implication is that the build-up of multivalent cation species in recycled process streams of low effluent bleach plants may decrease the solubility of oxidized lignin and negatively impact bleaching delignification.

## EXPERIMENTAL PROCEDURES

*Pulp Bleaching*

A conventional kraft pulp (southern pine) was obtained from a mill and used throughout this study. Additional details about the pulping conditions are provided in previous reports [5,12]. The $D_0$-stage was performed on a 29.3 kappa pulp at the following conditions: 1.79% $ClO_2$ on o.d. pulp (0.16 kappa factor), 3% consistency (100% aqueous), initial pH 4.2-4.6 prior to $ClO_2$ addition, 45°C, 30 minutes reaction time, and an end pH of 2.4. This treatment yielded a pulp with a kappa number of 19.5.

General caustic extraction conditions were as follows: 2.58% NaOH on pulp (0.55 caustic multiple), 10% consistency, 60°C, and 60 minutes reaction time. Extractions were

performed in Kapak®/Scotchpack heat-sealable pouches with various media. After extraction, the effluents were separated from the pulp fibers (prior to washing); the effluents were placed in an amber reagent bottle and stored at 5°C until needed. The pulps were washed with 130 mL/o.d. g of pulp of the corresponding medium (without alkali). Residual lignin content in the pulps was determined by micro-kappa number measurements (TAPPI Useful Method UM-246).

*Isolation of Oxidized Lignin from Caustic Extraction*

Approximately 150 o.d. g of a conventional softwood kraft pulp were bleached with an aqueous DE sequence, similar to the conditions listed above. The resulting pulp had a post-extraction kappa number of 8.5. The extraction effluent (~1.1 L) was separated from the pulp using a Büchner funnel and freeze-dried to yield ~1.9 g of organic material [12].

A sample of this material was subjected to an acid hydrolysis in accordance to TAPPI Standard T-249 cm-85 and the resulting hydrolyzate was analyzed for carbohydrates using HPLC [25]. A Bio-Rad "Polypore" HPX-87P (7.8 x 300 mm) and a Brownlee Labs 3-cm PPP-GU were used as the main and guard columms, respectively. Deionized NANOpure™ water was filtered through a 0.2 μm filter and degassed prior to being used as the eluant. The column was heated to 85°C and eluted with 0.6 to 1.0 mL/min water. A 20 mL aliquot of the hydrolzate was spiked with 2 mL of a 2 mg/L erythritol internal standard solution; the resulting solution was prepared for HPLC carbohydrate analysis according to the method developed by Kaar et al. [25]. Injections of 20 μL of the prepared solution were applied to the column and the elutions from the column analyzed by a refractive index detector operating at a range of 0.25 RIU. Results from the above analysis indicated that the isolated oxidized lignin contain ~7% carbohydrate material that was primarly composed of glucose, xylose and galactose monomeric units [12].

*Solubility Measurements*

A series of aqueous oxidized lignin solutions ranging from 0.015 to 0.15 g/L were made by using the above isolated, freeze-dried material. Absorbance measurements were made with these solutions, under alkaline conditions (~0.071 mol/L NaOH), using a spectrophotometer operating at a 260 nm wavelength. The amount of [L] (in g/L) was correlated with the 260 nm absorbance, $A_{260}$, using the Beer-Lambert relationship [12]. An absorptivity value for the oxidized lignin was determined to be 14.7 L/(g•cm) from the above calibration curve [12].

The solubility of the isolated lignin was measured in various ethanol-water and $BaCl_2$ solutions as follows. Approximately 25 mg of the freeze-dried material were weighed into a 5-mL volumetric flask. To this flask was added the alkaline medium of interest (~0.071 mol/L NaOH) to the mark. The contents of the flask were stirred at room temperature for 60 minutes. (A 60-minute stirring time was chosen based on the 60 minutes used for the E-stage.) Afterwards, the solution was centrifuged to remove any suspended solids. The supernatant was collected and diluted with ultrapure deionized (DI) water at several different concentrations. The $A_{260}$ values of the solutions were measured, and [L] was determined from the dilution factor. This was repeated in triplicate, and the reported solubility values are the averages. It was assumed that both the dissolved and undissolved components that comprise the oxidized lignin have the same absorptivity value. Reported solubility values had a coefficient of variation of ≤10%.

The [L] in the various E-stage effluents, produced from the earlier study [5,12], was determined as follows. Known volumes of the effluents were diluted with ultrapure distilled water (DI) to three different concentrations, and the $A_{260}$ values were determined. The average amount of [L] in the effluents was calculated from the $A_{260}$ and the dilution factor. Reported values had a coefficient of variation of ≤10%.

*Re-extraction of E-stage Pulps*

Pulps previously subjected to E-stages using either ethanol or aqueous 0.01 mol/L $BaCl_2$ solution as the extraction medium were used in these experiments. The pulps were washed with copious amounts of DI water prior to re-extraction. The washing process was observed to remove lignin only from pulps treated with an ethanol E-stage (Fig. 3). After washing, the pulps were re-extracted using an aqeuous E-stage at the same conditions as the first E-stage.

An acid-wash stage was performed on a 0.01 mol/L $BaCl_2$ E-stage pulp. The extracted pulp was diluted to 1% consistency with DI water that was acidified by concentrated HCl to 1.7 pH. The pulp was stirred for 2 hours at 80°C. Afterwards, the pulp was drained of the effluent and washed with 500 mL of DI water. The above procedure was repeated again. The effluents from the acid-wash were tested for dissolved $BaCl_2$ by the addition of concentrated $H_2SO_4$. A white precipitate (i.e., insoluble $BaSO_4$) was only observed in the first acid wash effluent; this indicated that most of the $Ba^{+2}$ in the fiber had been removed after the second wash stage. The above acid-washed pulp was subjected to a second E-stage with an aqueous medium at the same conditions as the first E-stage.

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## TABLES

Table I. Solubility of an alkali-treated $D_0$ lignin in various ethanol-water solutions under alkaline conditions (0.071 mol/L NaOH) and room temperature.

| EtOH Concentration (%, v/v) | Oxidized Lignin Solubility (g/L) |
|---|---|
| 0 | >22 |
| 50 | 2.79 |
| 65 | 0.806 |
| 75 | 0.250 |
| 100 | 0.0595 |

Table II. Solubility of alkali-treated $D_0$ lignin in various $BaCl_2$ solutions under alkaline conditions (0.071 mol/L NaOH) and room temperature.

| $BaCl_2$ Concentration (mol/L) | Oxidized Lignin Solubility (g/L) |
|---|---|
| 0 | >22 |
| $1.00 \times 10^{-2}$ | 1.62 |
| $1.75 \times 10^{-2}$ | 0.401 |
| $2.50 \times 10^{-2}$ | 0.309 |
| $5.00 \times 10^{-2}$ | 0.250 |
| $1.00 \times 10^{-1}$ | 0.221 |

Table III. Measured oxidized lignin concentration, [L], in effluents from E-stages [5,12], conducted in various ethanol-water media. Pre-extraction $D_0$-pulp had a kappa of 19.5.

| EtOH Concentration (%, v/v) | Post E-stage Kappa Number | [L] in E-Stage Effluent (g/L) |
|---|---|---|
| 0 | 9.3 | 2.22 |
| 50 | 10.6 | 1.37 |
| 65 | 12.4 | 0.860 |
| 75 | 14.4 | 0.266 |
| 85 | 15.7 | 0.0923 |
| 95 | 16.3 | 0.0766 |
| 100 | 16.3 | 0.0656 |

Table IV. Measured oxidized lignin concentration, [L], in effluents from E-stages [5,12], conducted in various $BaCl_2$ media. Pre-extraction $D_0$ pulp had a kappa of 19.5.

| $BaCl_2$ Concentration (mol/L) | Post E-stage Kappa Number | [L] in E-Stage Effluent (g/L) |
|---|---|---|
| 0 | 9.4 | 2.22 |
| $1.0 \times 10^{-3}$ | 10.1 | 1.91 |
| $2.5 \times 10^{-3}$ | 10.5 | 1.89 |
| $5.0 \times 10^{-3}$ | 11.8 | 1.37 |
| $1.0 \times 10^{-2}$ | 14.4 | 0.674 |
| $1.0 \times 10^{-1}$ | 15.5 | 0.217 |
| 1.0 | 15.3 | 0.240 |

Table V. Solubility of various carboxylic acids and corresponding sodium salts in water and ethanol [18,19].

| Carboxylic Acid/Na Salt | Solubility (g/L of Solvent) | | | |
|---|---|---|---|---|
| | Water | | Ethanol | |
| | -COOH | -COONa | -COOH | -COONa |
| Formic/Formate | miscible | 769 | miscible | slightly soluble |
| Benzoic/Benzoate | 16.6 | 556 | 435 | 13.3 |
| Salicylic/Salicylate | 2.2 | 1110 | 370 | 109 |
| Oxalic/Oxalate | 143 | 37 | 400 | insoluble |
| Succinic/Succinate | 77.9 | 200 | 54.1 | insoluble |

## FIGURE CAPTIONS

Figure 1. Comparisons of the effect of ethanol concentration on post-extraction kappa number (□, curve A), dissolved lignin concentration in the extraction effluents (◇, curve B) and oxidized lignin solubility (●, curve C).

Figure 2. Comparisons of the effect of $BaCl_2$ concentration on post-extraction kappa number (□, curve A), dissolved lignin concentration in the extraction effluents (◇, curve B) and oxidized lignin solubility (●, curve C).

Figure 3. The effect of aqueous washing and re-extraction on a $D_0$-treated pulp extracted with 100% ethanol medium.

Figure 4. The effect of aqueous washing, acid treatment and re-extraction on a $D_0$-treated pulp extracted with an aqueous 0.01 mol/L $BaCl_2$ medium.

Figure 1

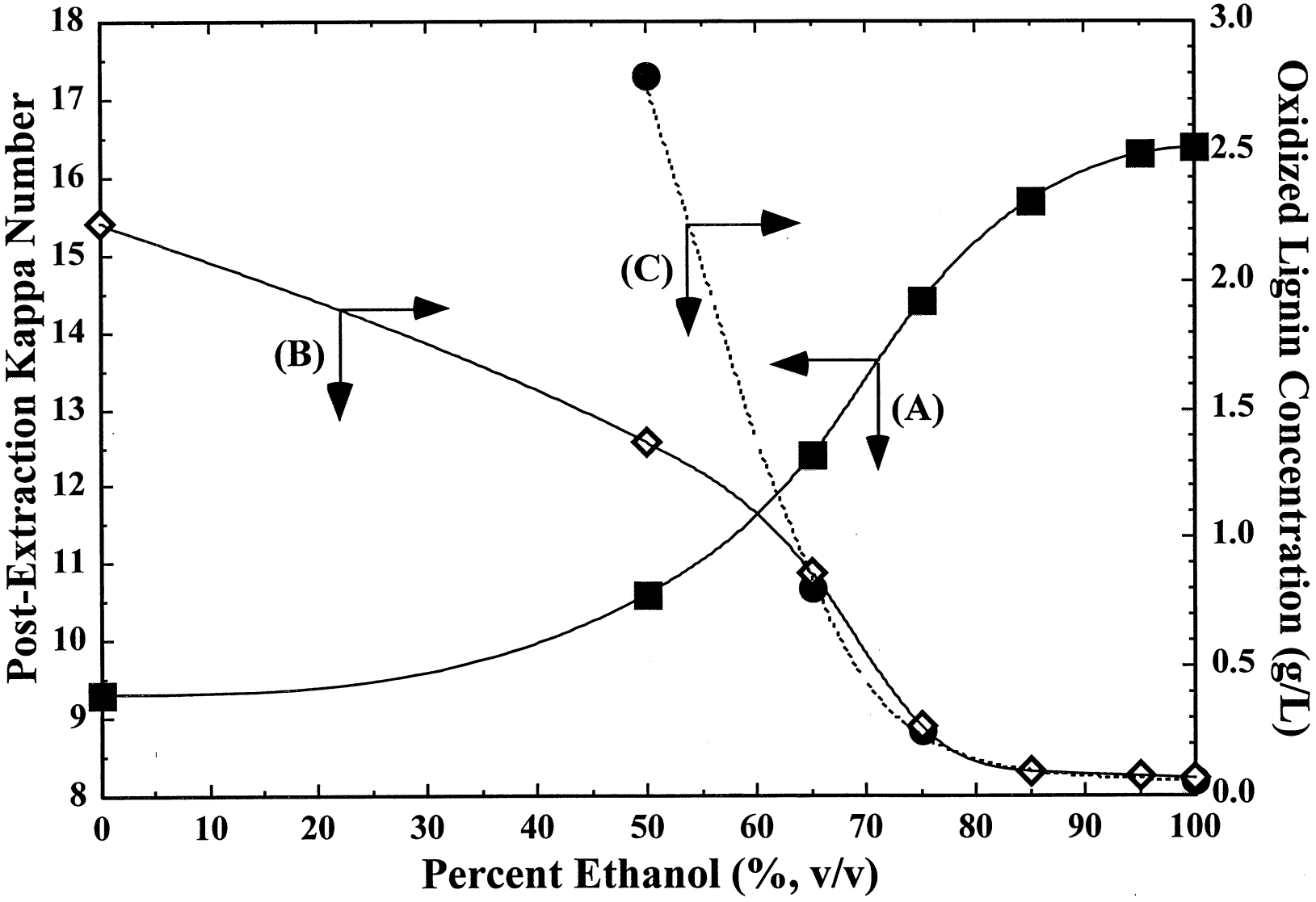

Post-Extraction Kappa Number
Oxidized Lignin Concentration (g/L)
Percent Ethanol (%, v/v)
(A)
(B)
(C)
18
17
16
15
14
13
12
11
10
9
8
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
10
20
30
40
50
60
70
80
90
100

Figure 2

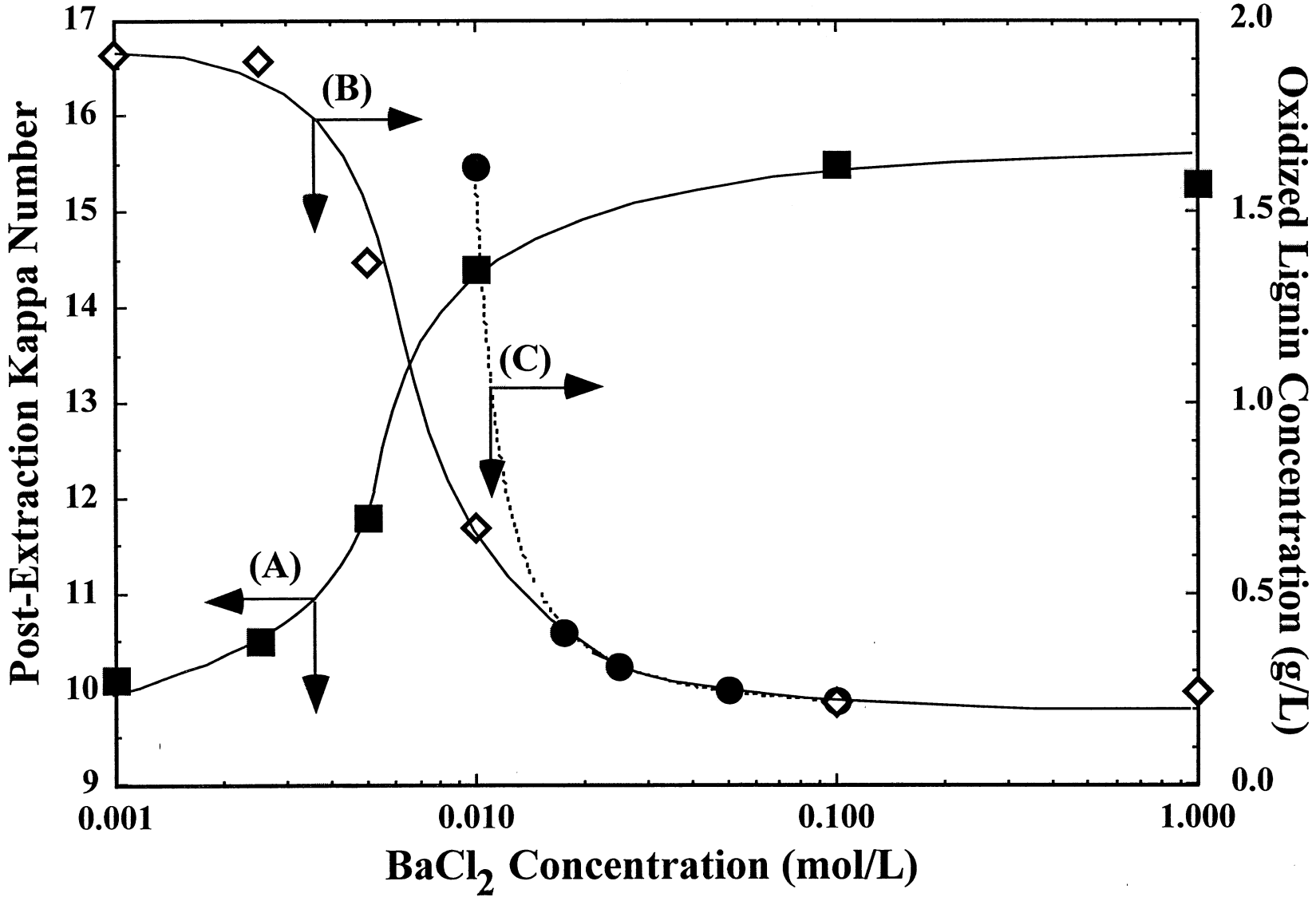
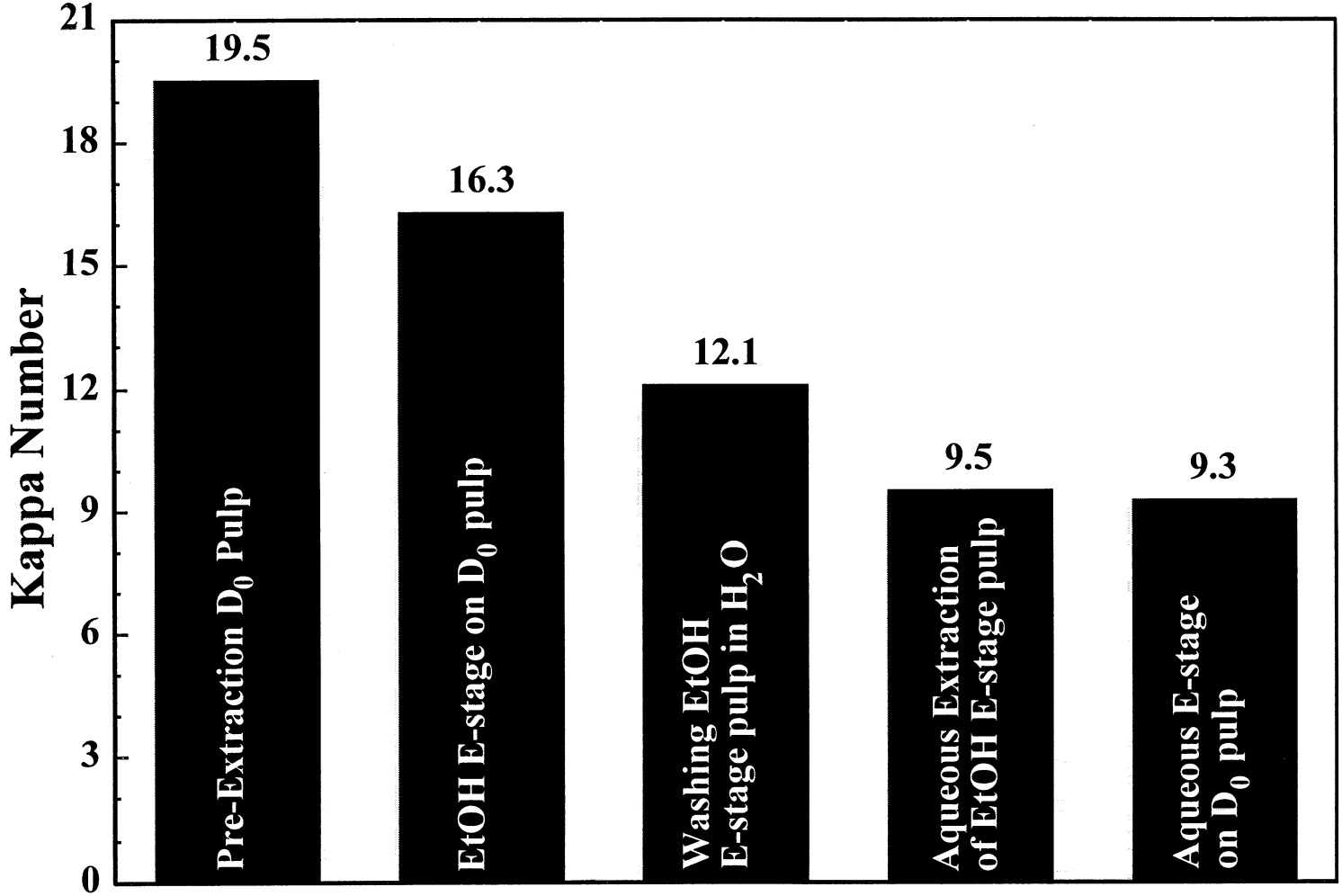

Post-Extraction Kappa Number
Oxidized Lignin Concentration (g/L)
BaCl2 Concentration (mol/L)
(A)
(B)
(C)
17
16
15
14
13
12
11
10
9
2.0
1.5
1.0
0.5
0.0
0.001
0.010
0.100
1.000

Figure 3


Kappa Number
21
18
15
12
9
6
3
0
19.5
16.3
12.1
9.5
9.3
Pre-Extraction $D_0$ Pulp
EtOH E-stage on $D_0$ pulp
Washing EtOH E-stage pulp in $H_2O$
Aqueous Extraction of EtOH E-stage pulp
Aqueous E-stage on $D_0$ pulp

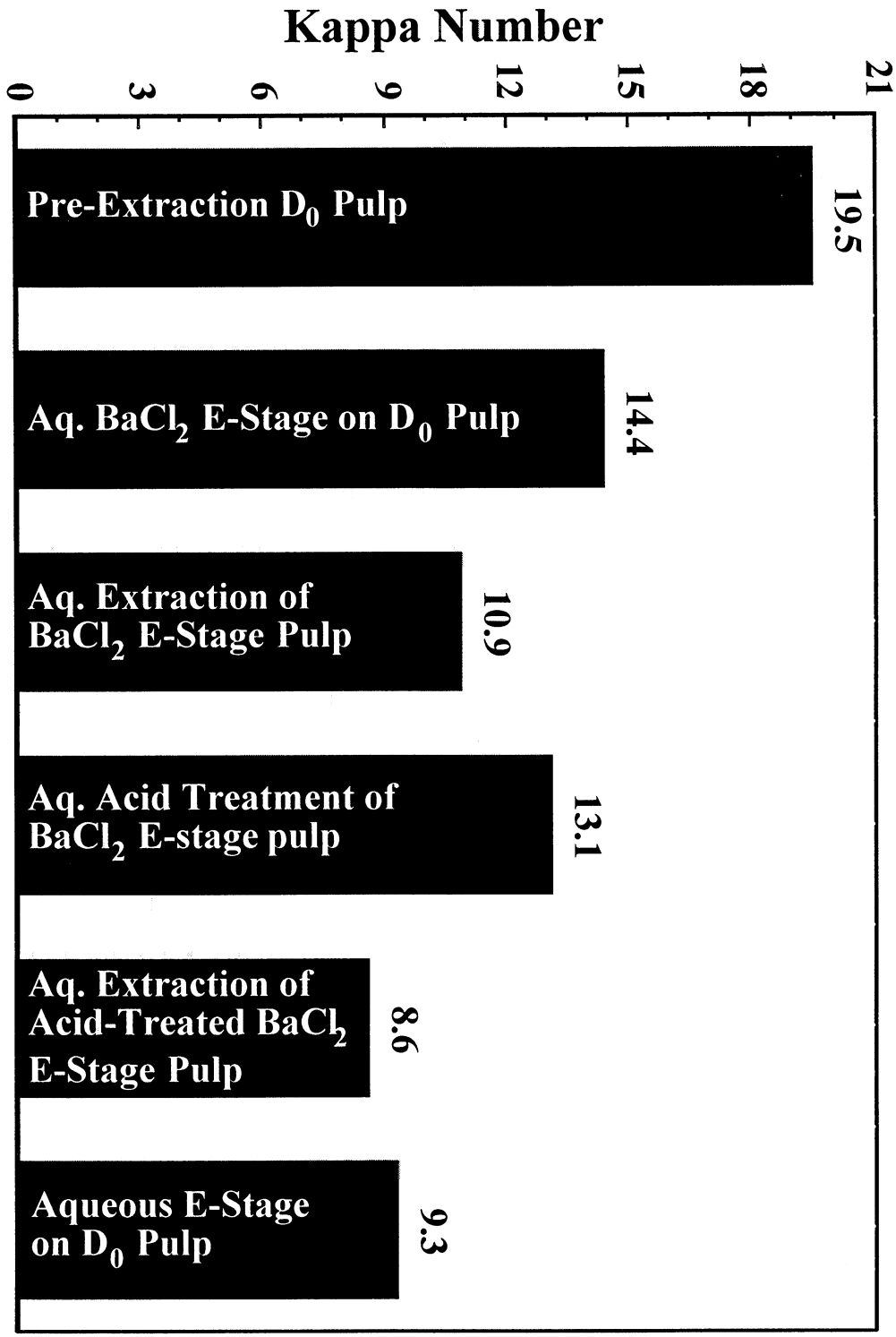

Kappa Number
0
3
6
9
12
15
18
21
Pre-Extraction $D_0$ Pulp
19.5
Aq. $BaCl_2$ E-Stage on $D_0$ Pulp
14.4
Aq. Extraction of $BaCl_2$ E-Stage Pulp
10.9
Aq. Acid Treatment of $BaCl_2$ E-stage pulp
13.1
Aq. Extraction of Acid-Treated $BaCl_2$ E-Stage Pulp
8.6
Aqueous E-Stage on $D_0$ Pulp
9.3

Figure 4